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Annual uptake of atmospheric CO₂ by the Weddell Sea derived from a surface layer balance, including estimations of entrainment and new production

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Abstract

Data from two cruises, one in April/May 1996 and one in December/January 1993, covering the same wide area in the offshore Weddell Sea, were used to derive the annual extent of entrainment and the capacity of the biological pump. The former property was obtained with the help of dissolved oxygen data, whereas the latter was approximated with nutrients. Especially the data from April/May, representing the initial state of the winter surface layer, were crucial to assess the annual extent of these processes. The results were applied to our carbon dioxide data. The annual increase of the Total CO₂ (TCO₂) concentration in the surface layer due to vertical transport amounts to 16.3 μmol kg⁻¹. An entrainment rate of deep water in the surface layer amounting to 35 ± 10 m yr⁻¹ was deduced. The compensating, biologically mediated TCO₂ reduction was calculated to be larger than the TCO₂ increase due to vertical transport. Since the balance of these two processes determines whether the Weddell Sea is a source or a sink of CO₂, this indicates that the Weddell Sea, albeit upwelling area, is definitely a sink for atmospheric CO₂ on an annual basis. This conclusion is further supported by contemplations that the biological drawdown of CO₂ in the Weddell Sea as a whole is probably underestimated by our calculations. The new production for the Weddell Sea on a per unit area basis was found to be much higher than that for the Antarctic Ocean, when the latter value is being obtained by traditional biological methods. On the other hand, the CO₂ uptake by the Weddell Sea on a per unit area basis is somewhat smaller than the CO₂ uptake by the world ocean. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Weddell Sea; carbon dioxide; sink; entrainment; new production

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1. Introduction

The key question for carbon cycling research in the Southern Ocean is whether this high latitude area, like the North Atlantic Ocean, is able to take up atmospheric carbon dioxide. In an attempt to tackle

this problem, many measurements of the partial pressure of CO_2 (pCO_2) in the surface water have been conducted from which air–sea fluxes were calculated. In the Antarctic Circumpolar Current a mosaic of source and sink sites for CO_2 was found (Inoue and Sugimura, 1988; Metzl et al., 1991; Poisson et al., 1993). Spatio-temporal variability of pCO_2 on all kinds of spatial and temporal scales is large (Poisson et al., 1993), suggesting that an intricate interplay of many different processes with varying rates governs the CO_2 distribution. In specific cases correlations have been found between pCO_2 and other properties, such as temperature, chlorophyll or even iron (Takahashi et al., 1993; De Baar et al., 1995; Bakker et al., 1997). Nevertheless, the annual cycle of CO_2 variation and the processes that govern it are still largely unknown. This highly complicates the estimation of the CO_2 source or sink function on an annual scale, which would require an immense effort of pCO_2 measurements.

In the Southern Ocean upwelling of the Warm Deep Water (WDW) occurs. The WDW is a deep water mass stemming from the other oceans and is accordingly CO_2 -rich. The CO_2 -elevating effect in the surface layer by the WDW has been well-known (Weiss et al., 1979; Takahashi et al., 1993). Another major agent in the CO_2 cycle is biological activity. Due to this the surface waters of the Southern Ocean show undersaturation in the summer and early autumn periods (Takahashi et al., 1993; Robertson and Watson, 1995; Schneider and Morlang, 1995). However, even in the productive season also supersaturation can be observed (Inoue and Sugimura, 1988). Most studies so far have demonstrated the qualitative and sometimes quantitative effects of the major agents in the carbon cycle, but always for a relatively short time span and small spatial extent.

In the present study we use a different, more quantitative approach to the carbon cycling in the Antarctic. Since upwelling and biological activity are in fact the major processes acting on the CO_2 content of the surface water, we concentrated on these two processes in the first place and then derived the CO_2 changes associated with them. The difference between the CO_2 changes due to these opposite processes determines whether the region is a source or sink for atmospheric CO_2 . Instead of pCO_2 we used total carbon dioxide (TCO_2) concentration data

to obtain a balance of CO_2 variations within the surface layer. With the aid of oxygen data of the WDW and the surface layer, the amount of WDW involved in upwelling was determined according to a method adopted from Gordon and Huber (1990), which was modified for our data set. The effects of biological activity on the CO_2 content were approximated using nutrient changes. The data are from a transect closing off the Weddell Sea basin, which was occupied twice. In a previous investigation we demonstrated the great potential of this method for the Weddell Sea (Hoppema et al., 1995). In the present study new, recent data are used which are crucial for incorporating all relevant processes to their full extent, that is, to obtain annual results. These include unique data from a transect in early winter when the area was fully ice-covered.

2. Methods and data

Most data presented are from a transect across the Weddell Sea (Fig. 1) occupied in April/May 1996 during cruise ANT XIII/4 (Fahrbach, 1997) of the icebreaker 'FS Polarstern'. Also some data from previous cruise ANT X/7 in December 1992/January 1993 (Fahrbach, 1994) are shown. At both of these cruises the same equipment was used. At all hydrographic stations water samples from all over the water column were collected with a 24-place rosette sampler which was equipped with a Conductivity Temperature Depth (CTD) instrument. Temperature data were obtained from the CTD. Its accuracy was set by shore-based calibration and is better than 3 mK. Salinity data appearing here were derived from bottle samples analyzed with an Autosol 8400B salinometer. All salinities are given on the Practical Salinity Scale. Further details on the hydrographic measurements were reported by Fahrbach (1997). Dissolved oxygen (O_2) was measured with a standard automated Winkler technique with photometric end-point detection, precision 0.2% CV.

In this paper the parameter representing the CO_2 system is the Total carbon dioxide (TCO_2) concentration, which was determined with a slightly modified standard coulometric technique (Stoll, 1994: Chap. 2). TCO_2 is the sum of all inorganic carbonate species dissolved in seawater (identical to DIC,

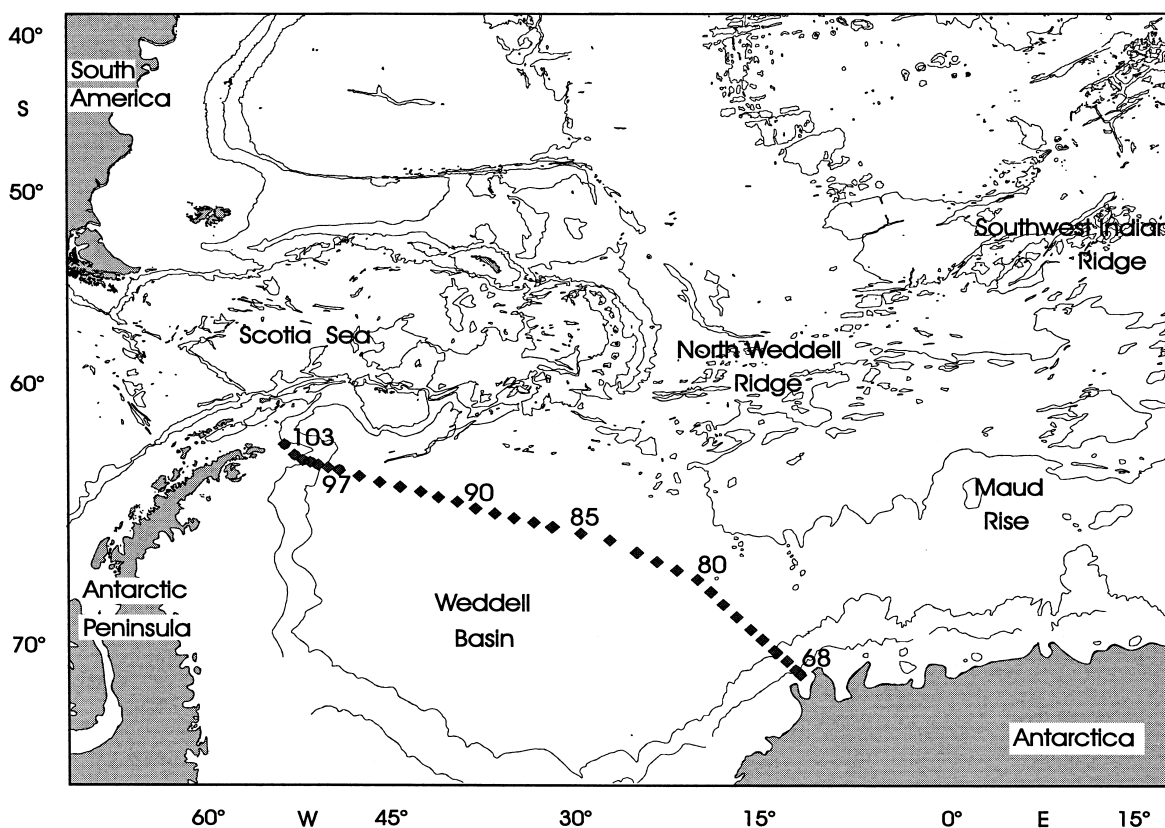


Fig. 1. Map of the Weddell Sea and adjoining regions with the location of the stations occupied during cruise ANT XIII/4 (1996) on the transect between Kapp Norvegia and Joinville Island at the tip of the Antarctic Peninsula. The same transect was occupied during summer cruise ANT X/7 (1992/1993).

ΣCO_2 and Total Carbonate). All analyses were performed within 24 h of sampling, during cruise ANT XIII/4 within 12 h. The precision, expressed by the mean of all duplicates on the section of cruise ANT XIII/4, amounts to $1.0 \mu\text{mol kg}^{-1}$. Standardization on both cruises was accomplished through certified reference seawater (DOE, 1994). For further details on the TCO_2 measurements refer to Stoll (1994).

Concentrations of nitrate and phosphate were determined by standard colorimetric methods using a rapid flow (60 samples/h) TRAACS autoanalyzer (Technicon). Daily diluted stock standards were used for calibration. As a reference standard, used for statistical purposes and data correction, a so-called cocktail (100-fold diluted) was used consisting of a mixture of phosphate, nitrate and silicate. The precision for nitrate and phosphate amounted to 0.21 and $0.03 \mu\text{mol dm}^{-3}$, respectively.

3. Large-scale distributions

In Fig. 2 vertical sections (upper 2000 m) of TCO_2 , dissolved oxygen and potential temperature (θ) are presented for the Weddell Sea between Kapp Norvegia and Joinville Island. This figure is a cross-section of the Weddell Gyre, the cyclonic structure dominating the water circulation south of the Atlantic sector of the ACC. Its volume transport is about 30 Sv of which 90% flows within the boundary current (Fahrbach et al., 1994). Off Kapp Norvegia water from the east enters the Weddell basin, where it is transported to the southwest, while off Joinville it flows to the northeast. In the centre of the gyre currents are weak and variable, albeit indications for persistent structures were also reported (Orsi et al., 1993; Fahrbach et al., 1994). The dominating structure of the gyre circulation pointing to

large-scale upwelling is particularly evident in the sections of potential temperature and dissolved oxygen (Fig. 2). The vertical sections of the nutrients nitrate and phosphate (not shown) roughly show the same features as the section of TCO_2 .

In the surface layer, which is about 100 m thick, minima of TCO_2 and θ and a maximum of O_2 were observed. The underlying layer is the Warm Deep Water (WDW) which is characterized by maxima of θ and TCO_2 and an O_2 minimum. WDW is essentially the only deep water mass that is injected into the Weddell Gyre. The lower boundary of the WDW can be detected by a weak TCO_2 maximum, albeit only in the margins of the gyre (Hoppema et al., 1997). It coincides approximately with the 0.2°C isotherm. Underneath the WDW the Weddell Sea

Deep Water is found in which gradients are small. The latter water mass is a mixture of WDW and the bottom water produced in the Weddell Sea.

In the western part of the basin the θ maximum has its lowest value ($\theta < 0.5^\circ\text{C}$). This is indicative of the centre of the gyre, an area with relatively weak motion and longer residence times. In this area the θ maximum has been eroded to the largest extent through mixing with water from above and below. The observed TCO_2 maximum values in this area are the highest of the entire section and the O_2 minimum values the lowest. This suggests that these extrema have been reinforced by remineralization of organic matter which produces CO_2 and consumes oxygen. Apparently, the relatively long residence time of the water in the central area enables an

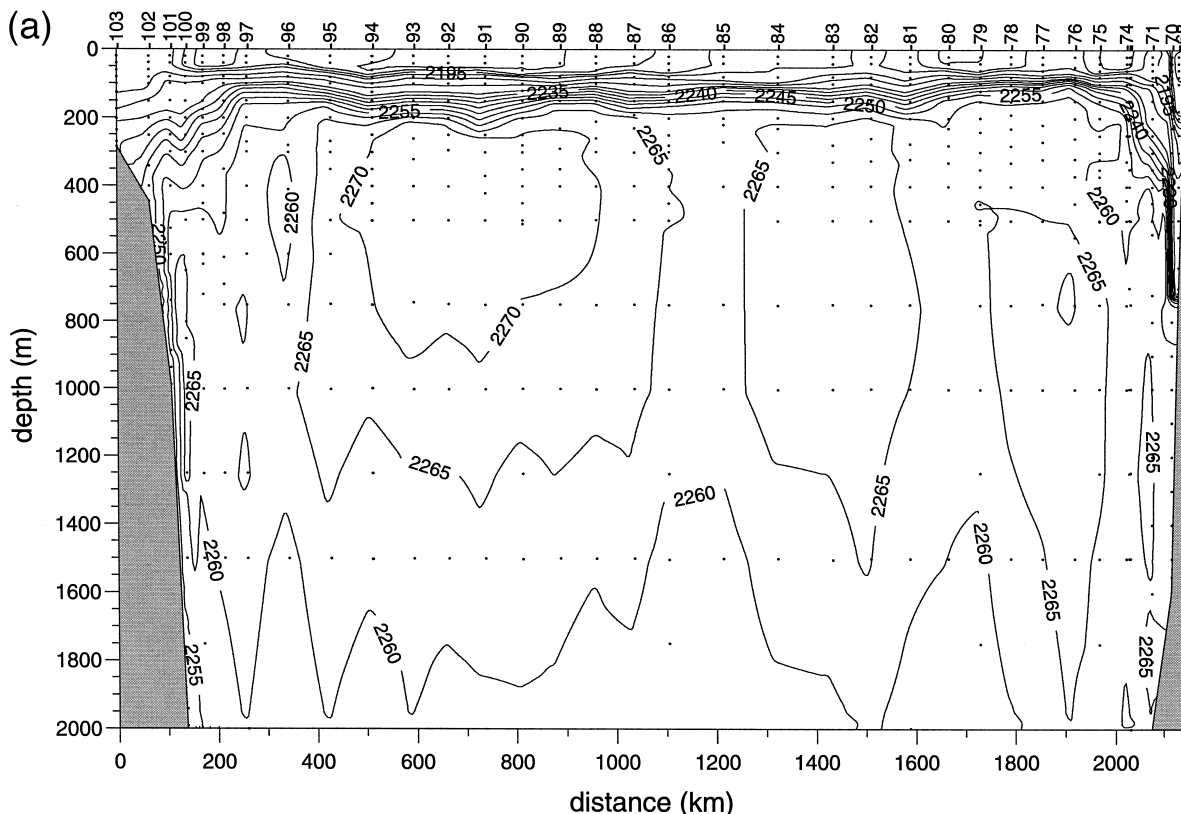


Fig. 2. Vertical sections of the upper 2000 m of the water column contoured for, (a) TCO_2 , (b) Dissolved oxygen, and (c) Potential temperature across the Weddell Sea between Kapp Norvegia (right) and Joinville Island (left). Data are from cruise ANT XIII/4 in April/May 1996.

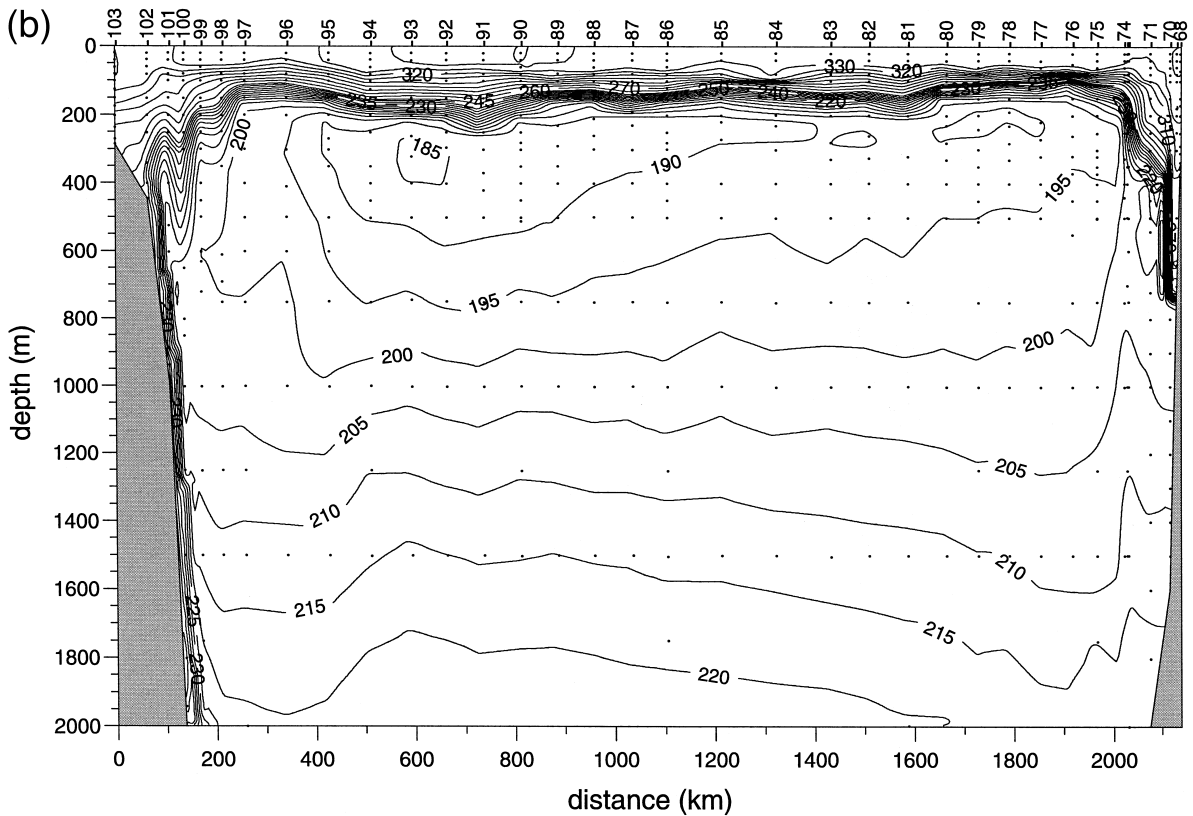


Fig. 2 (continued).

increase of the TCO_2 and a decrease of the O_2 concentration in the WDW.

4. Calculation of entrainment/upwelling

Upwelling of WDW into the surface layer is a continuous process which tends to make the surface layer shallower. Vertical diffusion weakens the gradient between the WDW and the surface layer. The balancing process for the two aforementioned ones, tending to deepen and sharpen the surface layer, is the entrainment of WDW. On an annual basis there is a balance between these processes (Gordon and Huber, 1990). As the vertical diffusion has a much smaller magnitude than upwelling and entrainment, this implies that upwelling and entrainment are approximately of the same magnitude. Note that both have the same dimensions. Entrainment is effected by turbulent action within the surface layer with

respect to an essentially non-turbulent subsurface layer (the WDW), for example through relative ice motion or thermohaline convection (Martinson, 1990). In principle, entrainment occurs all through the year, but it is most intensive during the winter due to the high wind speeds and the large air–sea temperature difference.

We will presume, after Gordon and Huber (1990), that the period of main entrainment starts at the onset of the winter sea ice cover and ends with the opening of the ice pack. During our cruise in the Weddell Sea in April 1996 the sea ice was in the process of being formed, making the April data perfectly suited to represent the initial conditions of the winter surface layer. The state of the surface layer in April is illustrated by Fig. 3, in which typical vertical profiles of TCO_2 are shown for April as compared to July (mid-winter), both in the central Weddell Sea. In April the winter mixed layer is being formed, where the lower range near 80 m displays concentrations

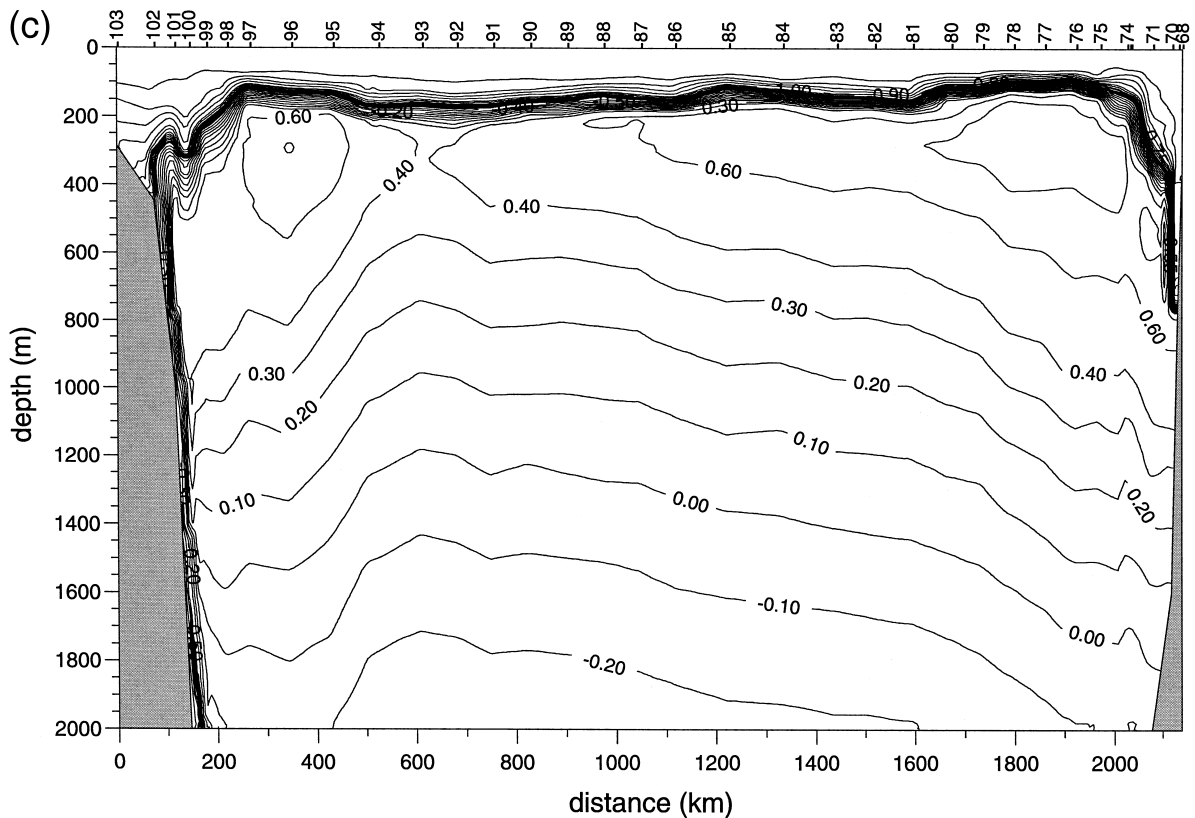


Fig. 2 (continued).

that point to significant incorporation of WDW. In contrast, in mid-winter the concentrations are uniform all through the 100 m mixed layer (Fig. 3). The state of the surface layer at the end of the winter can be extracted from data collected in December 1992/January 1993, albeit the latter are actually from early summer: a remarkable characteristic of the surface layer in early summer is the temperature minimum at its base (i.e., above the permanent pycnocline). The temperature minimum in Dec./Jan. was within 0.1°C of the temperature of the near-freezing winter surface layer, indicating that the temperature minimum layer is a remnant of the surface layer of the previous winter. Hence, data from the temperature minimum layer can be taken to represent the state of the winter surface layer at the end of the winter, i.e., at the end of the period of main entrainment. As our data of April and Dec./Jan. virtually envelope the period of main entrainment activity,

these are used to estimate the entrainment to its full annual extent.

The calculation of the total entrainment is performed by comparing property values in the surface layer at the start of the entrainment period with those at the end of this period. Temperature and salinity are less suitable for this purpose because they are non-conservative in the surface layer due to heat exchange with the atmosphere and ice formation/melting, respectively. The concentration of chemical properties might be influenced by freezing and melting of sea ice (represented by variations of salinity) which could bias the calculations. The relative variation of TCO_2 in the Weddell Sea is comparable with that of salinity, and therefore a significant part of the observed TCO_2 variation is due to gain or loss of fresh water. If, as in the case of O_2 , the relative variation is an order of magnitude larger than that of salinity, the contribution of freshwater variation to

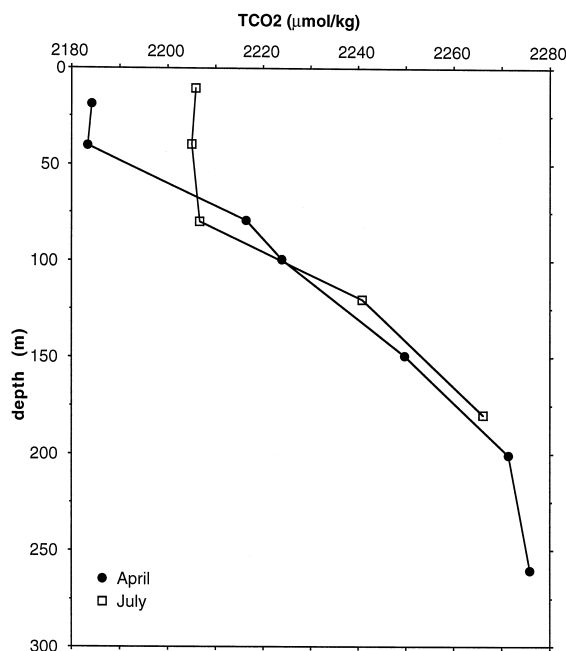


Fig. 3. Vertical profiles of TCO_2 in the central Weddell Sea in autumn (April 1996) and winter (July 1992) showing differences in the surface layer (< 100 m).

the overall O_2 variation is insignificant. This makes O_2 the most suitable tool for the calculation of entrainment.

Using O_2 for the calculation of the entrainment, the following assumptions are implicit: (1), the ice cover impedes the exchange of O_2 with the atmosphere; and (2), biological activity under the ice is negligible. As to (1), the Weddell Sea is completely ice-covered as of April which was verified during our cruise in April 1996. At the end of the ice-covered period, a seasonal pycnocline is formed within the surface layer, effectively separating the temperature minimum layer (which we use for the calculation) from the near-surface layer which is involved in air–sea exchange. Thus, possible air–sea exchange of O_2 after the opening of the ice-pack will not interfere with our entrainment calculations. As to (2) above, Gordon and Huber (1990) presented evidence, based on chlorofluorocarbon data, that O_2 behaves conservatively under the ice. In Table 1 surface layer and WDW data of O_2 (and for comparison also of TCO_2) are presented. These are averages of a section across the Weddell Sea (Fig. 2), exclud-

ing the margins. Note that the surface values for Dec./Jan. refer to the temperature minimum layer. Concentrations of TCO_2 and O_2 in the WDW were taken from the temperature maximum, except when a shallower extremum of these properties was observed. Usually, O_2 and TCO_2 either have an extremum coinciding with the temperature maximum, or the value at the depth of the temperature maximum is close to that of the extremum value. The entrainment is calculated through the fraction of WDW (F_{WDW}) needed to change the concentrations in the surface layer of April to those in Dec./Jan. and is extracted from the following equation:

$$F_{\text{WDW}} * [\text{WDW}] + (1 - F_{\text{WDW}}) * [\text{SW}(\text{April})] = [\text{SW}(\text{Jan.})] \quad (1)$$

where $[\text{SW}(\text{April})]$ is the surface water concentration in April, $[\text{WDW}]$ the concentration in the WDW, and $[\text{SW}(\text{Jan.})]$ the surface water (i.e., temperature minimum) concentration in Dec./Jan. Substituting the O_2 concentrations appearing in Table 1 (for $[\text{WDW}]$ the mean of April and Dec./Jan.) in Eq. (1), this yields 0.345 ± 0.062 for the WDW fraction. Since we presume to have captured nearly all entrainment activity during a whole year, this result says that within one year 34.5% of the surface layer is replaced by WDW from below. Thus, the mean age of the surface layer with respect to entrainment is about 2 years and 11 months (2.9 years). As the mean winter mixed-layer depth in the Weddell Sea is about 100 m, an entrainment rate of $35 \pm 10 \text{ m yr}^{-1}$ is obtained.

Two comments should be made to justify our calculations. First, the depth of the WDW core is 200–300 m, which is too deep to be tapped by the

Table 1

Mean oxygen and TCO_2 concentrations for the surface mixed layer and the WDW layer (temperature maximum) in the Weddell Sea (excluding the margins), which are used to derive the extent of entrainment of WDW into the surface layer. For Dec./Jan. the appropriate surface layer data are from the temperature minimum layer

	Oxygen ($\mu\text{mol kg}^{-1}$)		TCO_2 ($\mu\text{mol kg}^{-1}$)	
	Dec./Jan.	April	Dec./Jan.	April
Surface layer	286.0 ± 2.7	337.1 ± 4.3	2219.8 ± 2.6	2190.5 ± 7.0
WDW layer	190.5 ± 0.9	187.6 ± 1.9	2265.5 ± 2.5	2268.7 ± 3.9

surface layer by way of entrainment. The water that actually gets entrained has properties lying in between those of the WDW and the surface layer. However, our method calculates the total amount of WDW that has been transferred into the surface layer, independent of the way it has come there. In the end it is the 'pure' WDW that is transferred into the surface layer, and this is also the process that is of interest for the composition of the surface layer. Second, the data of April and Dec./Jan. are not consecutive, through which possible interannual variability may be introduced. The influence of this on the result is small. Interannual variation in the WDW exists but is minimal. Moreover, for the calculation of F_{WDW} the mean O_2 concentration in the WDW was taken. Also, the O_2 concentration of the surface layer in late autumn, early winter, when the ice pack is closing, is always close to saturation due to the intense exchange of O_2 between the ocean and the atmosphere.

5. Capacity of the biological pump of the Weddell Sea

Biological activity is a net remover of CO_2 and nutrients from the surface layer, in this context the term *biological pump* is commonly used. This is due to the fact that part of the organic material produced by the phytoplankton escapes the surface layer through various processes (e.g., settling of particles) and is either remineralized to CO_2 and nutrients at greater depths, or is deposited on the seafloor. Due to the specific hydrographic conditions (large-scale upwelling) in the Weddell Sea, with the surface layer ultimately deriving from the WDW, the capacity of the biological pump can simply be assessed. If the surface layer derives from the WDW, it should, without other processes exerting influence, have the same properties. To assess the capacity of the biological pump the concentrations of biologically mediated properties in the WDW and in the surface layer are compared.

If we want to apply this principle to assess the biological pump, the concentrations should not be influenced by other processes and the concentrations should be representative for a kind of steady state situation. The changes of CO_2 and O_2 in the surface

layer are not only the result of biological processes but also are brought about by interactions with the atmosphere. Therefore, for these gases this method is not valid without adaptation. In contrast, for the nutrients, which do not interact with the atmosphere (phosphate) or only negligibly (nitrate: via N_2 -fixation/denitrification) this method appears to be applicable. The nutrients can only be used when the seasonal cycle of primary production and remineralization within the surface layer is at rest (i.e., in the winter period), thus obeying the condition of having a steady state. The April data, representing the onset of austral winter, are perfectly suited for our purposes. In April biological activity in the surface layer is low, which is evidenced by low chlorophyll *a* values of $0.1\text{--}0.2 \mu\text{g dm}^{-3}$ (C. Dubischar, AWI, personal communication, 1996).

Average values for phosphate, nitrate and TCO_2 in the surface and WDW layers of the early winter-time Weddell Sea appear in Table 2. Since we presume that the surface layer is completely shaped by the WDW, it should, without other processes influencing it, have the same salinity as the WDW as well. However, the surface layer is less saline than the WDW (Table 2) due to excess precipitation and addition of glacial melt water. As the concentrations of the nutrients and TCO_2 are affected by the freshwater content of the surface layer, the data in Table 2 were normalized to a salinity of 35. The surface layer of the Weddell Sea is lower by 8.15 and $0.524 \mu\text{mol kg}^{-1}$ in nitrate and phosphate, respectively, than the WDW (Table 2). The ratio of these changes is 15.6 which is quite close to the classical $\Delta(\text{NO}_3)_{\text{bio}}:\Delta(\text{PO}_4)_{\text{bio}}$ ratio of 16 (Redfield et al., 1963). Evidence that the classical Redfield model is valid in the Weddell Sea was obtained from surface

Table 2

Mean values for the nitrate, phosphate and TCO_2 concentrations and for salinity in the surface and WDW (temperature maximum) layers of the Weddell Sea in April 1996. Values are normalized to a salinity of 35, i.e., multiplied by 35/S

	Surface layer	WDW layer
Nitrate ($\mu\text{mol kg}^{-1}$)	26.51 ± 1.41	34.66 ± 0.46
Phosphate ($\mu\text{mol kg}^{-1}$)	1.887 ± 0.095	2.411 ± 0.032
TCO_2 ($\mu\text{mol kg}^{-1}$)	2242.4 ± 12.1	2289.1 ± 4.2
Salinity	34.190 ± 0.075	34.688 ± 0.005

layer depletion data (Hoppema and Goeyens, 1999). We can thus conclude that the differences in nutrients between the surface and WDW layers are indeed caused by biological consumption in the surface layer, in fact justifying our assumptions for calculating the capacity of the biological pump. The mean age of the surface layer being 2.9 years (Section 4), the annual consumption of nitrate and phosphate through the action of the biological pump becomes 2.81 ± 0.32 and $0.181 \pm 0.022 \mu\text{mol kg}^{-1} \text{yr}^{-1}$, respectively.

6. Upwelling/entrainment versus the biological pump

Knowing the entrainment rate (Section 4) and the capacity of the biological pump (Section 5) in the Weddell Sea, these can be applied to derive the CO_2 changes in the surface layer associated with these counteracting processes. Hence, it is possible to settle which of the two processes has the largest impact on the CO_2 concentration.

The annual TCO_2 increase in the surface layer due to entrainment is calculated analogously to the calculations in Section 4. The TCO_2 concentration of the surface layer [SW] after the annual entrainment is extracted from:

$$[\text{SW}] = F_{\text{WDW}} * [\text{WDW}] + (1 - F_{\text{WDW}}) * [\text{SW}(\text{April})] \quad (2)$$

(see also Eq. (1)). The TCO_2 concentrations in the WDW ([WDW]) and in the surface water in April ([SW(April)]) are taken from Table 1, while F_{WDW} is 0.345 (Section 4). This yields $2216.9 \mu\text{mol kg}^{-1}$ for [SW]. Thus, the surface layer TCO_2 is annually increased through entrainment activity by $2216.9 - 2190.5 = 26.4 \mu\text{mol kg}^{-1} \text{yr}^{-1}$. In connection with this entrainment calculation an additional process that changes the TCO_2 concentration should be taken into consideration. Substituting the salinities in Eq. (2) the surface water value (April) of 34.190 (Table 2) would increase to 34.362 after entrainment. Thus, between the end of winter (after the entrainment period) and the next early winter (begin of the consecutive entrainment period) a freshening of the surface layer occurs which also reduces the concentration of TCO_2 . To arrive at the observed initial

TCO_2 concentration of the surface layer of $2190.5 \mu\text{mol kg}^{-1}$ after freshening, the actual TCO_2 concentration had been $2190.5 * (34.362/34.190) = 2201.5 \mu\text{mol kg}^{-1}$. Thus, the freshening caused a decrease of the TCO_2 concentration by $11.0 \mu\text{mol kg}^{-1} \text{yr}^{-1}$. Combining both of the above figures for entrainment and freshening, the net TCO_2 increase becomes $26.4 - 11.0 = 15.4 \mu\text{mol kg}^{-1} \text{yr}^{-1}$.

Since in steady state the mean TCO_2 concentration in the Weddell Sea surface layer is approximately constant from year to year, the above calculated TCO_2 increase of $15.4 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ must be compensated by an equally large decrease. (Actually, there is a small systematical increase of the TCO_2 concentration of the surface water due to the invasion of anthropogenic CO_2 from the atmosphere, which amounts to about $1 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ (Hoppema et al., 1998); the figure was deduced from an observed TCO_2 increase in the Weddell Sea Bottom Water). There is an independent way to check this annual TCO_2 decrease of the surface layer. This is done by comparing the TCO_2 concentration of the WDW and the surface layer. In contrast to the above calculated increase due to entrainment, the difference between WDW and the surface layer can actually be observed. However, the observed difference is a dynamical one, as it is generated every year again. Thus, the TCO_2 difference between the WDW and the surface layer is equal to the annual TCO_2 decrease in the surface layer. Calculating the TCO_2 difference from the April data (normalized) of the WDW layer and the surface layer (Table 2) and accounting for the age of the surface layer (2.9 years; Section 4) this results in $16.1 \mu\text{mol kg}^{-1} \text{yr}^{-1}$.

The calculated TCO_2 increase in the surface layer amounting to $15.4 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ is very similar to the decrease of $16.1 \mu\text{mol kg}^{-1} \text{yr}^{-1}$. Accounting for the small net TCO_2 increase of about $1 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ due to anthropogenic causes (Hoppema et al., 1998) the similarity is slightly less (the difference then being $1.7 \mu\text{mol kg}^{-1} \text{yr}^{-1}$). Thus the annual dynamical variation of TCO_2 in the surface layer lies between 15.4 and $17.1 \mu\text{mol kg}^{-1} \text{yr}^{-1}$. The good match between both calculated modifications of the surface layer puts confidence in the methods used.

Fig. 4 gives a schematic representation of the surface layer and the processes determining its TCO_2

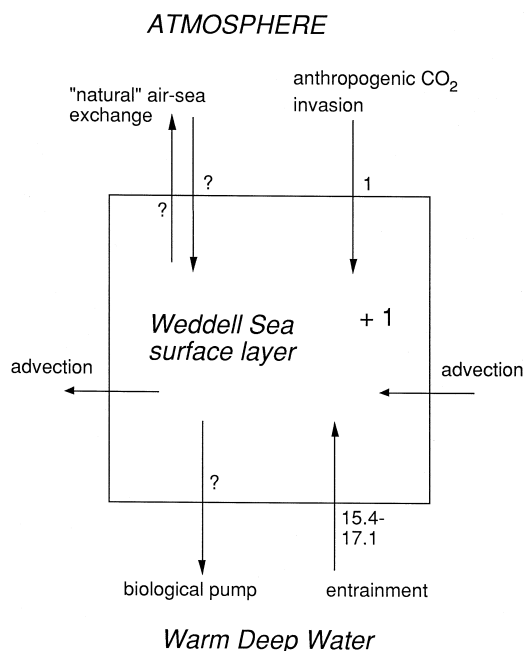


Fig. 4. Schematic representation of the surface layer of the Weddell Sea with processes (arrows) tending to change the TCO_2 concentration. The numbers denote changes of the TCO_2 concentration (in $\mu\text{mol kg}^{-1}$).

concentration. Apparently, if we know the amount of carbon involved in the biological pump, we obtain, by difference, an estimate for the CO_2 exchange between the Weddell Sea surface layer and the atmosphere. However, this only holds when advection can be neglected, i.e., when the amount of TCO_2 advected into the surface box is approximately equal to the amount leaving the box (Fig. 4). Several strong indications can be found that advection is unlikely to bias the results of our analysis. First, the Weddell Gyre is a divergent feature, which possesses the characteristic that a net water movement occurs away from the centre, making it highly improbable that there would be a net advection towards the central part of the gyre. Second, the net effect of advection is zero when the concentrations of the parameters concerned are the same in the central Weddell Sea and in the boundaries. Actually, our oxygen and TCO_2 data show that this is the case. The mean of oxygen and TCO_2 as appearing in Table 1 is from a homogeneous area in the central Weddell Sea. On both sides of it there is a strip of > 100 km from

which the data were not included in the mean of Table 1. Still, the values for oxygen and TCO_2 in the surface layer in this strip are about equal to those in the central part (not the concentrations in the WDW, though, which was a priori the reason to lay the bound right at this position). Moreover, the current speeds in the central Weddell Sea are very small, which renders it impossible for water from the margins to reach the central part. A tentative calculation may illustrate this. With current speeds of $0\text{--}0.6$ cm s^{-1} (Fahrbach et al., 1994), the typical distance the surface water travels during the period of main entrainment (7 months) is of order $0\text{--}100$ km. These currents have varying directions, further diminishing the net effect of advection. Such a distance is much shorter than the length of our transect (about 1000 km) or the extend of the central Weddell Sea itself (> 2000 km). That the residence time of the water in the central Weddell Sea is relatively long can also be deduced from the occurrence of TCO_2 -enriched sub-surface layers (Hoppema et al., 1997). Third, as part of our calculation of the biological pump the ratio of changes of nitrate to phosphate was found to agree well with the theoretical Redfield ratio (Section 5). Larger deviations from this ratio are generally observed when advection would determine the changes in nutrients. Fourth, an inverse model of the Weddell Sea (Yaremchuk et al., 1998), fed with TCO_2 data, suggests that the advective budget of CO_2 is closed.

As discussed previously, it is impossible to assess the capacity of the biological carbon pump straightforwardly. However, we can come to an indirect estimation using the results for phosphate and nitrate (Section 5) and the appropriate Redfield ratios between carbon and these nutrients. In Table 3 results are presented for the amount of carbon as calculated with different sets of Redfield ratios. Our choice of these ratios is prompted by the following deliberations: many modifications of the original ratios of Redfield et al. (1963) have been published. However, most of these relied on methods that were not sufficiently accurate. Recently a comprehensive study by Anderson and Sarmiento (1994), using sophisticated analytical methods, essentially confirmed the original Redfield ratios in the deep world ocean. The ratios determined in that study are currently considered the best available. Also for the surface layer of

Table 3

Calculation of the net biological carbon consumption (the biological carbon pump) in the Weddell Sea surface layer from the consumptions of nitrate and phosphate, using different Redfield ratios from the literature

Annual net biological nitrate consumption: $2.81 \pm 0.32 \mu\text{mol kg}^{-1} \text{ y}^{-1}$.

Annual net biological phosphate consumption: $0.181 \pm 0.022 \mu\text{mol kg}^{-1} \text{ y}^{-1}$.

	Calculated net biological carbon consumption ($\mu\text{mol kg}^{-1} \text{ y}^{-1}$)
<i>Redfield et al. (1963)</i>	
C/N = 6.6	18.5 ± 2.1
C/P = 106	19.2 ± 2.3
<i>Anderson and Sarmiento (1994)</i>	
C/N = 7.3	20.5 ± 2.3
C/P = 117	21.2 ± 2.6
Average	19.9 ± 2.4

the Weddell Sea the original Redfield model appears to be valid (Hoppema and Goeyens, 1999). From Table 3 it becomes clear that the TCO_2 decrease in the surface layer as a consequence of the biological pump is comparable to the amount of TCO_2 involved in entrainment as calculated above. The final value for the net biological carbon consumption is the average of all values derived from the Redfield et al. (1963) and the Anderson and Sarmiento (1994) ratios, and it amounts to $19.9 \pm 2.4 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$ (Table 3). Thus, the biological carbon pump is significantly larger than the amount of entrained TCO_2 , allowing the conclusion that the offshore Weddell Sea is a sink for atmospheric CO_2 on an annual basis.

A summary of all contributions to the changes of the TCO_2 concentration appears in Table 4. Also the total amounts for the entire offshore Weddell Sea

(surface area $1.7 \times 10^{12} \text{ m}^2$) are presented. The amount of TCO_2 involved in entrainment was taken to be the average of the two calculated values at the beginning of this section. The entry for biological activity is taken from Table 3. We arrive at a total uptake by the Weddell Sea proper of $0.8 \cdot 10^{13} \text{ g C yr}^{-1}$. Note that the balance in Table 4 describes the TCO_2 changes due to the three processes: entrainment, biological activity and air–sea exchange. The actual fluxes of TCO_2 are much larger. For instance, the actual upwelling of 1.9 Sv of WDW (see Section 7.1 below) with a TCO_2 concentration of $2267.1 \mu\text{mol kg}^{-1}$ yields a flux of $1.6 \cdot 10^{15} \text{ g C yr}^{-1}$. The major part of this upwelled CO_2 is transported out of the Weddell Sea by advection within the Ekman layer.

7. Discussion and conclusions

7.1. The Weddell Sea a CO_2 sink

Our results give credit to the notion that the capacity of the biological pump as a means of carbon reduction in the surface layer is larger than the tendency of carbon increase through vertical transport (upwelling), notably on an annual basis. As a consequence of this the Weddell Sea is invoked to be a net sink for atmospheric CO_2 . Our calculations are pertinent to the offshore Weddell Sea, which being an open ocean region of the Antarctic Ocean has a

Table 4

Annual balance of the surface layer (mean depth 100 m) of the offshore Weddell Sea. In the second column the mean concentration differences caused by these specific processes and in the third column the integrated changes over the whole Weddell Sea (surface area $1.7 \cdot 10^{12} \text{ m}^2$ between South Sandwich Islands and Kapp Norvegia). Atmospheric exchange is the closing entry, determined by difference. A plus sign means increase in the surface layer

	($\mu\text{mol kg}^{-1}$)	($10^{13} \text{ g C y}^{-1}$)
Entrainment	$+16.3 \pm 0.9$	$+3.4 \pm 0.2$
Biological activity	-19.9 ± 2.4	-4.2 ± 0.5
Atmospheric exchange	$+3.6 \pm 3.3$	$+0.8 \pm 0.7$

relatively low primary production (El-Sayed, 1984). Despite its low productivity the biological carbon pump in the offshore Weddell Sea is strong enough to more than compensate the action of the vertical transport. Considering that the CO_2 uptake by the Weddell Sea is largely brought about by the biological drawdown of CO_2 and the biological activity in the margin area is higher than in the open ocean (Bodungen et al., 1986; Holm-Hansen and Mitchell, 1991), we conclude that by extrapolating our result for the offshore area to the entire Weddell Sea, we probably underestimate the effect of the biological pump. Hence, our value of the CO_2 sink for the Weddell Sea as a whole (as given in Table 4) may be a lower bound.

Previous investigations in the Southern Ocean have highlighted sink and source areas of CO_2 . These results were necessarily only valid for the limited time span in which the pCO_2 measurements were performed, and this time span was mostly restricted to the austral summer period. Our findings are supported by accompanying pCO_2 data from the Weddell Sea, which suggest that the Weddell Sea absorbs CO_2 in autumn and early winter because of intensive cooling (Stoll et al., 1998) and in summer as a consequence of intensive biological activity (Hoppema et al., 1995). By the end of winter or early spring a slight supersaturation may exist in parts of the Weddell region (Bakker et al., 1997). Data from other investigators collected on several cruises and in different seasons reveal that the Weddell region is mostly undersaturated in summer whereas in winter both undersaturation and supersaturation is observed (Takahashi et al., 1993).

The total CO_2 uptake by the Weddell Sea, amounting to $0.8 \cdot 10^{13} \text{ g C yr}^{-1}$, is only 0.4% of the total uptake by the world oceans, the latter being about $2 \cdot 10^{15} \text{ g C yr}^{-1}$ (Siegenthaler and Sarmiento, 1993). On a per unit area basis the CO_2 uptake by the Weddell Sea is only 84% of the global ocean CO_2 uptake. The reason for this lesser uptake of course is the upwelling of CO_2 -rich deep water occurring in the Weddell Sea. The uptake of CO_2 by the Weddell Sea is both biologically and physically mediated and both are also intertwined. It should be realized that the uptake of atmospheric CO_2 by the Weddell Sea does not only pertain to the anthropogenic CO_2 . Provided steady state, the calculated

uptake is more of a compensation for ocean regions where, predominantly due to (more) intensive upwelling activity, the pCO_2 in the surface layer is so high that CO_2 is outgassed to the atmosphere. As such, it is part of the natural carbon cycle. The most important of such source regions is the equatorial region (Postma, 1964). Nevertheless, due to the elevated level of CO_2 in the atmosphere, part of the CO_2 invading the Weddell Sea is of anthropogenic origin.

7.2. Entrainment / upwelling

As touched upon in Section 4 we calculate the entrainment of WDW but the water that is actually entrained into the surface layer originates from the pycnocline. This pycnocline water has a higher O_2 concentration than the WDW. Thus, to attain the observed decrease of the O_2 concentration in the surface layer in the winter period (which was used to calculate the fraction of admixed WDW), a larger amount of pycnocline water is needed than of pure WDW. The consequence is that when an entrainment rate is calculated based on the presumed entrainment of pure WDW, this necessarily is an underestimation. On the other hand, the derived entrainment rate could be considered to be scaled to entrain pure WDW. For our purposes this is in fact the property we are interested in. For clarity we should emphasize that the calculated amount of TCO_2 transferred into the surface layer through vertical transport (Section 4) is not affected by the entrainment rate because in these calculations the calculated fraction of WDW is used. Neither the conclusions about the CO_2 sink function of the Weddell Sea are affected.

Our entrainment rate of $35 \pm 10 \text{ m yr}^{-1}$ is comparable to a previous estimate, amounting to 30 m yr^{-1} for a small area in the central Weddell Sea (Hoppema et al., 1995). For the latter estimate more assumptions were made, in particular because the initial state of the surface layer was not known due to the absence of the April data. Gordon and Huber (1990) reported an entrainment rate of 45 m yr^{-1} for the Weddell area at the prime meridian. This estimate is also based on a single cruise. For all these estimates the same restrictions hold as for the value obtained in the present study.

It is useful to calculate the total upwelling of the offshore Weddell Sea. We have to restrict our esti-

mation to the offshore region because near the continental slope and shelf the upwelling is not solely caused by large-scale divergent motion like in the central Weddell Sea. The surface area of the Weddell Sea west of the line connecting the South Sandwich Islands with Kapp Norvegia, but excluding the shelf areas, is $1.7 \cdot 10^{12} \text{ m}^2$. The total annual upwelling in this region is calculated from: $0.345 \times 100 \text{ m} \times 1.7 \times 10^{12} \text{ m}^2$, which equals 1.9 Sv ($1 \text{ Sv} = 10^6 \text{ m}^3 \text{ s}^{-1}$). Note that this calculation uses the fraction of WDW so our estimate gives the real amount of upwelled WDW. This figure may be compared with an estimate of the transformation rate of deep water to surface water for the area south of the line Kapp Norvegia-Joinville Island, amounting to 2.2 Sv (Fahrbach et al., 1994). Yaremchuk et al. (1998) obtained a smaller rate of 1.5 Sv by applying CTD data from several cruises and a different approach to reconstruct the currents in the near-surface layers. The fair correspondence with figures obtained with completely different methods is a further indication for the reliability of our approach. It should be noted however, that two factors complicate the comparison. First, our estimation of WDW upwelling is related to the open ocean area of the Weddell Sea and does not account for the upwelling at the shelf break, in contrast to the estimation of Fahrbach et al. (1994) and Yaremchuk et al. (1998). The shelf water ultimately originates from the WDW as well, and upwelling of WDW is thought to occur at the shelf break (Jacobs, 1991). Second, part of the upwelled water in the central Weddell Sea is directly involved in the process of bottom and deep water formation. This fraction of the upwelling does not appear in the estimates by Fahrbach et al. (1994) and Yaremchuk et al. (1998). These two factors act in opposite direction and thus partly cancel out.

7.3. Biological activity

From Table 4 the total biologically mediated drawdown of CO_2 for the Weddell Sea can be taken, which is $4.2 \cdot 10^{13} \text{ g C yr}^{-1}$ (surface area $1.7 \cdot 10^{12} \text{ m}^2$). This figure represents the net change of TCO_2 after one year of action of the biological pump and thus should be regarded as the 'new production', i.e., that part of the total primary production that is available for export out of the surface layer (Dugdale and Goering, 1967). Our new-production estimate

for the Weddell Sea may be compared with values reported for the Southern Ocean. Smith (1991) gives a value for the Antarctic Ocean proper, that is, the area south of the Polar Front (surface $38.1 \cdot 10^{12} \text{ m}^2$), amounting to $0.47 \cdot 10^{15} \text{ g C yr}^{-1}$. Chavez and Toggweiler (1995), making a crude physical estimate of new production in the Southern Ocean, arrived at a value of $1.1 \cdot 10^{15} \text{ g C yr}^{-1}$ (surface area $77 \cdot 10^{12} \text{ m}^2$). On a per unit area basis the new production of the Weddell Sea is 2 and 1.7 times as high as the estimates by Smith (1991) and Chavez and Toggweiler (1995), respectively. This implies either that the new production in the Weddell Sea is indeed twice as high as it is on average in the Southern Ocean, or that these previous values are underestimates. For our estimate of new production holds that it can be regarded as a combined spatio-temporal integration covering large parts of the basin. It is known that such estimates tend to be higher than those based on traditional biological methods (Jennings et al., 1984), because the latter methods cannot sufficiently account for the seasonal variation and the large natural patchiness of biological processes. The discrepancy between our value and that by Smith (1991) may (partly) be caused by this effect. On the other hand, the estimate by Chavez and Toggweiler (1995) is by virtue of its way of calculation better comparable with ours. These authors came to their result through a large-scale comparison of the concentrations in the upwelled and downwelled waters in the Antarctic, and applied it to the entire surface area of the Southern Ocean, that is, the area south of the Subtropical Front. However, downwelling occurs at the Polar Front and using the surface area south of this front applied to their analysis would about double their value for the new production (per unit area). In that case the estimate for the new production in the Weddell Sea would agree quite well with the mean value for the Antarctic Ocean. Thus, the new production in the Weddell Sea is probably not very different from the average new production in the Antarctic Ocean. The fact that from a biological point of view the Weddell Sea is characteristic for the Antarctic Ocean is further indicated by the satellite-derived pigment concentration in the Weddell Sea, which, being a measure for the biological activity, about equals the mean of the Southern Ocean (Comiso et al., 1993).

7.4. Concluding remarks

We were able to determine the effects of upwelling and the biological pump on the CO₂ budget of the surface layer for a relatively large area like the offshore Weddell Sea. By difference we also obtained an estimate of the CO₂ air–sea exchange, allowing the conclusion that the upwelling area Weddell Sea, which moreover is commonly thought to be less productive, is a CO₂ sink. An important aspect of our results is that they are on an annual basis. We came to these results using the data of only two cruises. It is also possible to determine the annual air–sea exchange conducting measurements of the partial pressure of CO₂ (pCO₂) in the surface water and in the atmosphere. However, a much larger logistic effort (that is, many cruises) would be demanded because the seasonal and spatial variation of the surface water pCO₂ is very large. Applying budget-based calculations to other coherent regions of the Antarctic Ocean will lead to a reliable assessment of the extent of CO₂ air–sea exchange and requires a relatively moderate logistic effort.

It should be realized that the budget method is only a tool to obtain quantitative data on CO₂ fluxes. It does not provide insight into the processes causing these fluxes. These processes may be variable due to varying external factors, which would also cause variation of the associated CO₂ fluxes. To appropriately assess the possible variability of the CO₂ fluxes, process studies are required, in which pCO₂ measurements take a central position.

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